

# Characterization of Biodegradable Composite Films Prepared from Blends of Poly(Vinyl Alcohol), Cornstarch, and Lignocellulosic Fiber

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Several composite blends of poly(vinyl alcohol) (PVA) and lignocellulosic fibers were prepared and characterized. Cohesive and flexible cast films were obtained by blending lignocellulosic fibers derived from orange waste and PVA with or without cornstarch. Films were evaluated for their thermal stability, water permeability and biodegradation properties. Thermogravimetric analysis (TGA) indicated the suitability of formulations for melt processing, and for application as mulch films in fields at much higher temperatures. Composite films were permeable to water, but at the same time able to maintain consistency and composition upon drying. Chemical crosslinking of starch, fiber and PVA, all hydroxyl functionalized polymers, by hexamethoxymethylmelamine (HMMM) improved water resistance in films. Films generally biodegraded within 30 days in soil, achieving between 50–80% mineralization. Both starch and lignocellulosic fiber degraded much more rapidly than PVA. Interestingly, addition of fiber to formulations enhanced the PVA degradation.

**KEY WORDS:** Composite; mulch film; renewable resources; fillers; poly(vinyl alcohol); biodegradation; lignocellulosic.

## INTRODUCTION

Plastic materials are commonly used in agricultural practices for a variety of applications that include mulch films, greenhouse construction materials, packaging materials, etc. [1]. Conventionally, such plastics are manufactured from petroleum derivatives that are not degradable and persist in the environment long after their useful life is over. As a result, interest in the use of naturally degradable and/or biodegradable polymers for plastic manufacturing, particularly for use in agriculture, has grown considerably in recent

years [2,3]. Efforts have been made to develop environmentally compatible plastic products by incorporating renewable polymers as an alternative to petroleum-derived chemicals [4,5]. The renewable polymers are relatively inexpensive, environmentally friendly, and also naturally biodegradable. Particularly, plant material derived from renewable crops, by-products or their industrially processed wastes, offer a good source of fiber for applications [6].

Ongoing research cooperation between USDA laboratories and the University of Pisa, Italy has yielded several composite blends of poly (vinyl alcohol) (PVA) and lignocellulosic fibers derived from the wastes from industrially processed sugarcane, apple, and oranges [7]. Particularly, PVA is well suited for blends with natural polymers since it is highly polar and can also be manipulated in water solutions [8–10].

Globally, efforts are being made to develop bioplastics from renewable polymers for use as mulch film,

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materials for green-house construction, packaging, and aids for transporting and transplanting plants/seedlings. To succeed in such endeavors, fundamental knowledge pertaining to material properties and characterization is essential. For example, mulch film applied in the field will be subjected to prolonged exposure at relatively high temperature, which would necessitate that the thermal stability of polymers and composites be evaluated. This is especially important where compression and injection molding is used in material processing and product development.

This paper describes composite cast films prepared from blends of lignocellulosic fiber and PVA. Films were cast from aqueous suspensions with or without hexamethoxymethylmelamine (HMMM) present as a crosslinking agent. Urea and glycerol were added as plasticizers in the formulation. Additionally, cornstarch was also added to the formulations to further increase the content of renewable polymers, and to reduce the overall cost of the product, as cornstarch is a relatively inexpensive polymer derived from a surplus commodity. The composite films and their parent components were evaluated for their thermal properties, water permeability, and the effect of crosslinking with HMMM. Biodegradability of films in compost was tested in respirometric soil burial tests by measuring the net CO<sub>2</sub> production of the composites and their individual polymeric components (PVA and additives).

## MATERIALS AND METHODS

### Materials

Polyvinyl alcohol (PVA, Airvol 425) was purchased from Air Products & Chemicals Inc., Allentown, PA. PVA Airvol 425 was 95.5–96.5% hydrolyzed with an average molecular weight of 100,000–146,000. Hexamethoxymethylmelamine (HMMM, Cymel 303) is a low imino melamine-formaldehyde crosslinking agent with a D.P. of 1.75 and an average degree of methylation of 97% and

was purchased from Cytec Industries, Inc., Wallingford, CT. Citric acid was obtained from Aldrich Chemical Company, Milwaukee, WI. Glycerol and urea were purchased from Fisher Chemicals, Fairhawn, NJ, and Sigma Chemical Company, St. Louis, MO, respectively. Unmodified commercial-grade cornstarch (Buffalo 3401) with approximately 30% amylose and 70% amylopectin content was obtained from CPC International, Inc., Argo, IL. Orange fibers (OR) were the remains of fruit residue after juice extraction supplied by Sunflo Cit-Russ Limited, Lahore, Pakistan, milled and sieved to obtain 0.188 mm size particles. The OR composition was: 18% Cellulose, 13% protein, 15% crude fiber, 7% fat, 5% lignin, 11% ash, 21% hemicellulose and/or pectins and 10% moisture.

### Sample Preparation

A predetermined amount of PVA was added to water to achieve a solution of 10% solid content. The mixture was slowly heated to about 90°C with stirring until a homogeneous solution was formed. Water was added to compensate for any moisture loss that may have occurred during the heating process. In a 250 mL beaker, about 62 g of PVA solution was introduced and the desired amount of glycerol, urea, starch and water was added (by weight) to bring a final concentration equivalent to 10% solids. The resulting mixture was first heated at 80°C for 30 min under stirring and 6.2 g of OR was added. The mixture was stirred for an additional 10 min.

For crosslinked samples, a desired amount of HMMM and a catalytic amount of citric acid as indicated (Table I) were also added in formulations and the resulting mixture was stirred at 70°C for 45 min. After cooling at room temperature, 3 drops of BYK-019 aqueous defoamer was added and the mixture was further stirred for 5 min. Table I provides the description of blends and their compositions.

**Table I.** Composition of Composite Films

Sample	PVA (wt-p)	Fibers (wt-p)	Gly (wt-p)	Urea (wt-p)	Starch (wt-p)	HMMM (wt-p)	CitAc (wt-p)
PSt	100	—	50	50	50	—	—
PStX	100	—	50	50	50	29	2.9
PORSt	100	100	50	50	50	—	—
PORStX	100	100	50	50	50	29	2.9
POR	100	100	50	50	—	—	—

Gly, Glycerol; HMMM, hexamethoxymethylmelamine; CitAc, citric acid; wt-p, weight parts.

Samples: P, PVA; St, starch; X, crosslinked; POR series based on orange fibers (OR) as filler; G, glycerol; U, urea.

To prepare films, about 17 g of aqueous suspension (as described above) was poured onto a polypropylene plate (8 × 8 cm) and left to dry overnight at ambient temperature (23–24°C) and finally for 3 h in an oven at 50°C. The average thickness of films was about 50 µm.

### Thermogravimetric Analysis (TGA)

A Mettler TA4000 System consisting of TG50 furnace, M3 microbalance, and TA72 GraphWare was used for thermogravimetric measurements. Samples (about 10 mg) were heated from 25 to 600°C at a 10°C/min scanning rate, under nitrogen atmosphere (flow rate about 200 mL min<sup>-1</sup>). The onset temperature ( $T_{on}$ ) was determined as the temperature corresponding to the crossover of tangents drawn on both sides of the decomposition trace and the residue was evaluated as the residual weight at 600°C.

### Water Permeability

Water permeability was assessed by using 6 cm diameter Fisher Payne permeability cups containing 5 mL of water, sealed with the selected films. Caps were stored in a conditioned room (23°C and 50% RH) and variation in water weight with time was recorded. Tests were performed in triplicate. Three caps were sealed with polyethylene (PE) as the negative reference.

### Film Deterioration in Soil

From the cast film, 3 × 3 cm squares were cut and placed on the top of agricultural soil in a 6 × 6 cm pot. The pot was covered with a plastic net and exposed to atmospheric conditions for 4 months from May 21, 1999 to September 21, 1999 in the

vicinity of the Faculty of Chemistry, University of Pisa, Pisa, Italy. Variations in film morphology and the time by which films disintegrated, and weight loss were recorded. To determine the weight loss in specimens, films were first dry cleaned with a brush and the weight was recorded. A specimen of each sample was quickly washed in cold water and then the sample was dried in an oven at 70°C to constant weight. The weights of the sample, before and after washing were recorded.

### Soil Burial Respirometric Test

About 500 mg sample of each film was cut into small pieces (2 × 2 mm) and mixed with 25 g of compost soil in the 250 mL volume reaction chamber. The chamber was connected to a closed-circuit Micro-Oxymax Respirometer (Columbus Instruments, Columbus, OH) equipped with expansion interface, condenser and a water bath thermostated at 25°C. The cumulative CO<sub>2</sub> evolution was recorded every 6 h. Experiments were carried out over a period exceeding 55 days.

### Fourier Transformed Infrared (FTIR) Spectroscopy

Test samples (Table II.) were pulverized with KBr and pressed into transparent disks for analysis by FTIR spectroscopy. FTIR spectra were measured on a FTS 6000 spectrometer (Bio-Rad, Digilab Division, Cambridge, CT) equipped with a DTGS detector. The absorbance spectrum (4000–400 cm<sup>-1</sup>) of each blend or composite was acquired at 4 cm<sup>-1</sup> resolution and signal averaged over 32 scans. Interferograms were Fourier transformed using triangular apodization for optimum linear response. Spectra were baseline corrected and scaled by normalization on the methylene band

**Table II.** Thermal Parameters of Individual Components

Material	Volatiles (%)	$T_{on}$ (°C)	Peak 1		Peak 2		Residue (%)
			T (°C)	WL (%)	T (°C)	WL (%)	
OR	5	193	249	23	305	43	29
PVA	2	266	317	76	412	17	3
Starch	7	277	296	81	—	—	12
Glycerol	1	170	247	99	—	—	0
Urea	1	169	221	64	348	35	0

OR, Orange fibers;  $T_{on}$ , onset temperature; Peak 1, first decomposition peak; Peak 2, second decomposition peak; Residue, residue weight % at 600°C; T, temperature; WL, weight loss.

( $2930\text{ cm}^{-1}$ ) to adjust for differences in sample weights.

## RESULTS AND DISCUSSION

### Composition of Composites

A total of five selected formulations were prepared. All formulations contained PVA, glycerol and urea (Table I). In some blends, either starch, orange fiber or both were incorporated. In some formulations, PVA was either crosslinked with starch alone or together with the orange fiber using HMMM as a crosslinking agent and with citric acid present as a catalytic agent. In a previous study, composites prepared from PVA and lignocellulosic fillers indicated some promising properties [11]. This report further expands on those earlier observations to include chemical crosslinking via HMMM of hydroxyl functionalized polymers, namely PVA, starch and lignocellulosics in blends and evaluated the effect on their thermal properties and biodegradability due to the crosslinking.

### Thermal Characteristics

Thermogravimetric analysis (TGA) of the samples was performed to define the thermal stability of the starting raw materials and the films obtained from the casting of water suspensions of the blended materials. Data indicated two decomposition steps recognizable in the curve for OR fibers at 249 and

$305^\circ\text{C}$  (Fig. 1). The presence of such multiple decomposition peaks for OR fiber is not surprising as it is very much in accordance with the composite characteristics of the materials. Additionally, PVA, starch, glycerol, and urea were also individually analyzed for their thermal stability, as the thermal decomposition of the prepared blends will ultimately be influenced by the stability of each component present in the mixtures (Table II). After water loss, for PVA the decomposition mostly occurred in two steps, and  $T_{\text{on}}$  was at  $266^\circ\text{C}$ . Both starch and glycerol exhibited a single decomposition peak with their respective  $T_{\text{on}}$  at  $277$  and  $170^\circ\text{C}$ . Urea decomposed in two steps and the  $T_{\text{on}}$  was at  $169^\circ\text{C}$ .

In a PVA/starch/fiber blend (PORSt), after a water loss of about 4%, three degradations peaks were observed at  $221$ ,  $320$  and  $408^\circ\text{C}$ . The  $T_{\text{on}}$  was evaluated to be at  $168^\circ\text{C}$  (Fig. 2). The observed decrease in thermal stability for the PORSt composite is possibly due to the initial decomposition of low molecular weight components such as urea and glycerol. Thus, low decomposition temperatures for glycerol and urea must be taken into account when the materials containing these components are processed at high temperature. Despite the observed decrease in thermal stability, the PORSt blend retained the characteristics of thermoplastics materials and can still be useful for applications such as mulching films, packaging, etc., where melt processing of PVA, starch and fiber based mixtures is desirable.

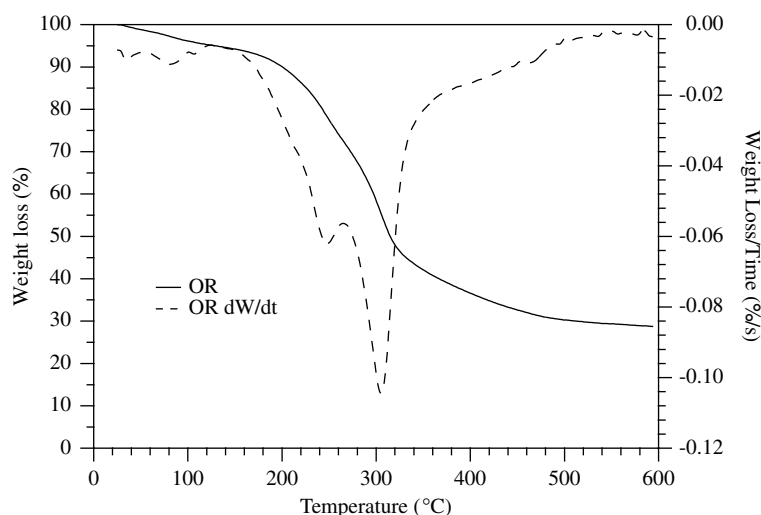


Fig. 1. Decomposition curve and first derivative of curve for OR.

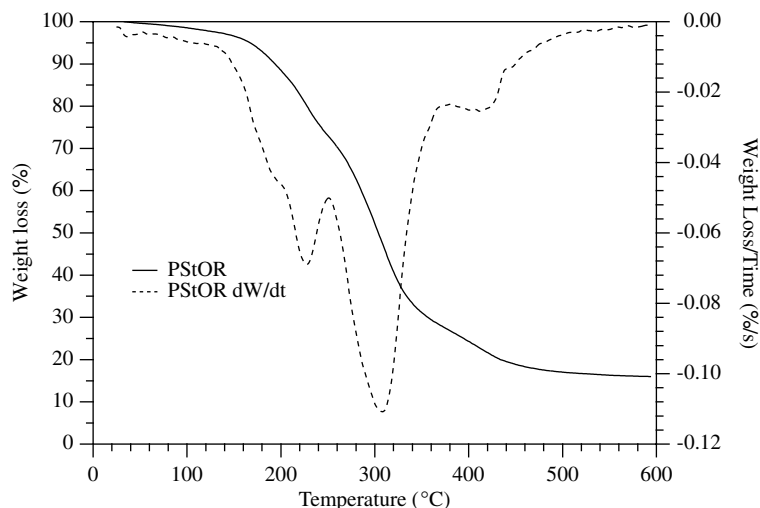


Fig. 2. Decomposition curve and first derivative of curve for PORSt.

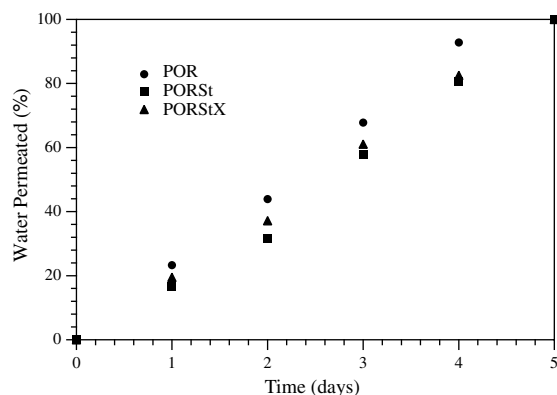


Fig. 3. Water permeability characteristics of POR, PORSt, and PORStX films.

### Water Permeability

Experiments were conducted to measure the water permeability of cast films based on POR, PORSt and PORStX formulations (Fig. 3). All samples were conditioned at 50% RH (23°C) for one week prior to their use in experiments. PE film was used as a control, which showed no water permeability. Permeability was expressed as % weight-loss of water in time. Results presented in Fig. 3 indicated that all of the composite films tested showed strong water permeability characteristics, and by the end of five days all films showed over 75% water loss. Film plasticized with glycerol and urea but not containing any starch (POR) showed the highest water permeability. Water permeability was relatively much slower in both PORSt and PORStX films. Unex-

pectedly, no significant difference in water permeability was recorded between the uncrosslinked (PORSt) and crosslinked (PORStX) films. Though all films became softened due to the water absorption, they appeared to be intact, retaining most of their consistency and cohesiveness. Expectedly, the crosslinked films did not gain much weight due to water absorption, but allowed water to permeate freely.

### Film Deterioration in Soil

The crosslinked as well as uncrosslinked film samples of PSt and POR were exposed to soil for 120 days under prevailing environmental conditions. The specimens of film samples were applied on the top of the soil surface. Under rainy conditions, water permeated through the films causing them to swell and become soft. However, the performance of films in maintaining the moisture and cohesiveness of the soil was not impacted, and upon drying films looked normal. After 120 days of exposure in soil, films eventually diminished in size and appeared hard and fragile (Fig. 4). Film deterioration was also accompanied by loss in their mechanical properties (not shown) as well as loss in their total weight after soil exposure (Table III).

The values representing the weight losses in films were probably underestimated as soil debris strongly adhered to the film surface. In general, all formulations lost weight close to 50%, the only exception being the crosslinked film (PORStX) which showed only 41% weight loss. Thus, crosslinking appears to slow the rate of film deterioration. Infrared analyses

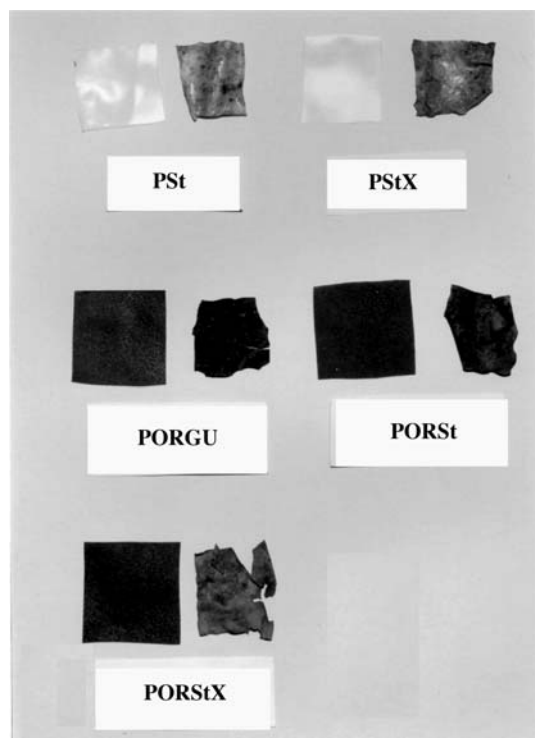


Fig. 4. PSt, PStX, POR, PORSt, and PORStX before and after exposure to soil for 120 days.

have been performed on the recovered samples. Figure 5 shows the FTIR spectra for PSt, PORSt and PORStX. The samples were compared by examining spectra that were normalized to the methylene peak at  $2930\text{ cm}^{-1}$  to show relative changes in peak heights before and after burial in soil for 120 days. All the recovered samples showed reductions in the hydroxyl absorbances ( $3500\text{--}3100\text{ cm}^{-1}$ ) due to degradation of the starch. The peak ratios indicate the starch degradation was greater in the uncrosslinked composite (PORSt) than in the crosslinked composite (PORStX) as expected. Interestingly, the presence of ligno-

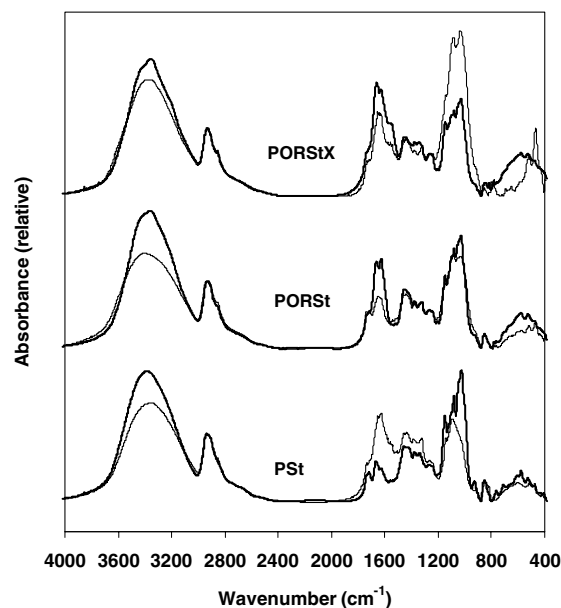


Fig. 5. FTIR spectra of PSt, PORSt and PORStX before (—) and after (---) soil burial.

cellulosic OR in the composites appears not to have greatly affected the extent of the starch degradation.

### Biodegradability

To test for biodegradability, specimens were examined for  $\text{CO}_2$  production and mineralization of carbon resulting from the microbial activity in soil. In control experiments, to determine the effect of each additive individually, the amount of sample used was proportional to the representative weight of each component in the blend. For example, in a blend of PORSt, roughly 500 mg of material was used in experiments of which about 350 mg was from the ORSt and the other 150 mg was contributed from the PVA. Thus, the ORSt and PVA controls contained equivalents of 350 and 150 mg sample, respectively. The  $\text{CO}_2$  produced by PVA alone was essentially similar to the background (uninoculated soil) control (Fig. 6). Much higher mineralization was observed in PORSt sample (uncrosslinked) compared to PORStX, the sample containing 8% crosslinker (Fig. 6). The  $\text{CO}_2$  production was much higher in PORSt blend compared to ORSt blend without PVA, suggesting that PVA degradation was stimulated by the presence of OR and St fillers in the blend. The PVA degradation stimulated by the presence of starch has been reported earlier for starch containing PVA composites exposed in the compost and the tropical

Table III. Weight Loss in Composite Films Exposed to Soil for 120 Days

Sample	Weight loss <sup>a</sup> (%)	Weight Loss <sup>b</sup> (%)
PSt	42 ± 2	47
PStX	48 ± 3	51
POR	46 ± 2	51
PORSt	41 ± 1	48
PORStX	35 ± 4	41

<sup>a</sup>Recovered from the soil and cleaned with a brush.

<sup>b</sup>After washing in cold water.

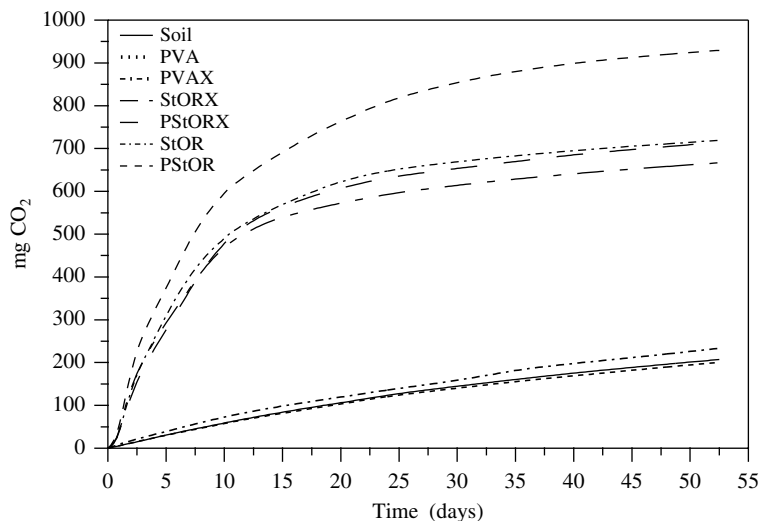


Fig. 6. CO<sub>2</sub> production of soil (control), PVA, PVAX, PORSt, ORSt, PORStX and ORStX.

marine environments [12,13]. This implies that mechanisms by which microorganisms and/or enzymes degrade complex biopolymers are quite complex. Peanasky et al. [14] have shown that in a starch-polyethylene blends, little starch was degraded if the concentration of starch fell below the percolation threshold for a cubic lattice or, in other words, the volume fraction of cubes at which all cubes are connected by at least one face-to-face contact. It is possible that starch in the starch-PVA matrix is quickly degraded initially, but once the concentration reached below the percolation threshold, microbes switched to another and more abundant and easily accessible carbon source like PVA. The amount of CO<sub>2</sub> released from the additives (ORSt, ORStX) exceeded the value corresponding to 100% mineraliza-

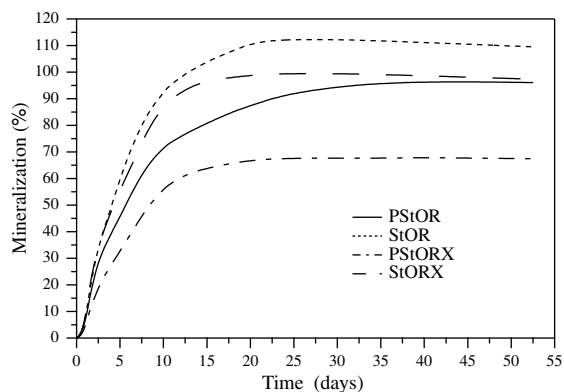


Fig. 7. Mineralization rate of PORSt, ORSt, PORStX and ORStX.

tion (Fig. 7), indicating that starch, along with other additives such as urea and glycerol, readily provided carbon and nitrogen sources which enhanced the mineralization capacity of the soil. This “priming effect” is already well documented in the literature [15,16]. For a similar reason, initially all samples with glycerol, urea and starch degraded more readily, and a much higher mineralization activity was recorded for these components compared to samples with lignocellulosics (OR). Mineralization for both cross-linked and uncrosslinked PVA remained roughly 2%. The poor mineralization for PVA in soil was also observed in earlier studies [17–22], and was attributed to the absence of PVA-degrading microorganisms in soil. On the other hand, PVA has been shown to degrade quickly in aqueous medium enriched with PVA-degrading microbes [23] but it degrades poorly when exposed to unpolluted water environment [24]. All blends achieved high mineralization values (50–80%) within 30 days.

After 30 days, fragments of degraded film samples were recovered and analyzed by FTIR spectroscopy. Figure 8 shows the FTIR spectra for PVA, PVAX and PORStX. Comparison of these samples by examining the spectra normalized to the methylene peak reveals that, PVA was slightly degraded after biodegradation in compost soil. Spectra of crosslinked PVAX showed evidence that it is more resistant to biodegradation than uncrosslinked PVA. The crosslinked composite PORStX showed about the same large amount of biodegradation in compost soil after 30 days as in regular soil after 120 days.

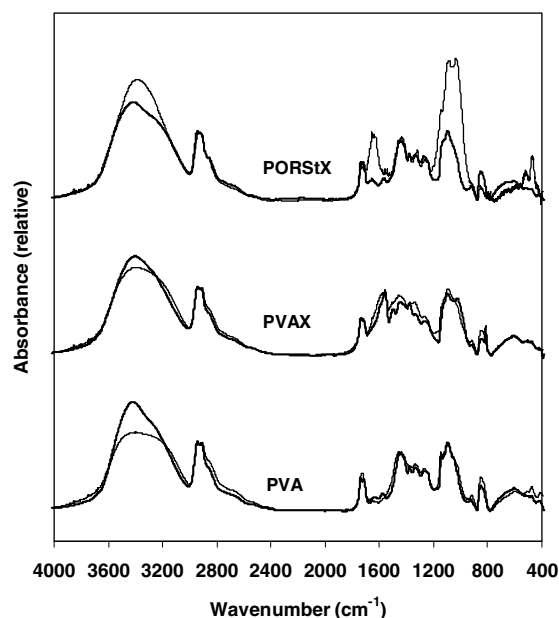


Fig. 8. FTIR spectra of PVA, PVAX and PORStX before (—) and after (---) biodegradation in compost soil.

## CONCLUSION

The thermal stability of PVA appeared to be appreciably larger than that of OR fibers as expected from their respective chemical structures. However, the POR blend exhibited only a modest decrease in the decomposition temperature compared to pure PVA, indicating its suitability for several practical applications. In spite of the hydrophilic character of PVA, starch and orange fiber, the water permeability and soil burial tests suggest that the composites will be able to both allow water to permeate easily and maintain the moisture content of the soil. The addition of a crosslinker in formulations lowered the overall extent of degradation in composites. Interestingly, CO<sub>2</sub> production was significantly higher in blends with PVA than without PVA, suggesting that the presence of starch and orange fiber stimulates PVA degradation in soil.

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## ACKNOWLEDGEMENTS

Research was done as a collaboration between the University of Pisa, Italy and the Plant Polymer Research Unit, USDA-ARS-NCAUR, Peoria, Illinois. The authors thank Ms. Paulette Smith, Ms. Jan Lawton and Mr. Gary Grose for technical assistance. The financial support for Ms. Patrizia Cinelli's Ph.D thesis research was provided by the Ministry of University and Technology of Italy, and in part by the USDA. The Sunflo Citrus Limited, Pakistan, provided gratis the orange waste by product for this study under the auspices of the United Nations Development Program for Pakistan. The assistance of the USDA International Program Office for arranging Dr. Patrizia Cinelli's visit to NCAUR is greatly appreciated.

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